

MOLTEN CARBONATE FUEL CELL WITH WATER INJECTION

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1. INTRODUCTION

Since the end of the 19th century, using the chemical oxidation energy of fossil fuels has been considered in order to produce electrical energy directly from fuel cells.

The fact that a cell is more easily supplied with a gas especially a carbon containing gas has lead engineers to be interested for a long time in molten carbonates as an electrolyte. The first works of Ostwald (1) then those of Baur (2) and his co-workers were concerned with cells using gases which contain hydrogen and carbon monoxide.

Davyan (3) then Broers and Ketelaar (4) recommended a molten electrolyte fixed in a porous solid matrix. Gorin (5), Justi (6) and more recently many others such as Hart (7) and Salvadori (8) have also recommended the use of molten carbonates in fuel cells.

An important improvement has been brought forward these last few years, especially by Broers, in the performance of molten carbonate cells by adding carbon dioxide to oxygen feed.

2. USE OF AN ELECTROLYTE BUFFER

Several goals of our research group have been aimed at understanding the mechanism of exchange in the molten carbonates and the functioning of oxygen and hydrogen electrodes.

The carbonate solvent is entirely dissociated into the anion CO_3^{2-} and cations and the anion CO_3^{2-} is further dissociated according to the equilibrium:



The system $\text{CO}_3^{2-}/\text{CO}_2$ can thus be considered an acid-base system according to Lux (9) and Flood and Förland (10) with exchange of the O^{2-} ions.

To the equilibrium [1] there corresponds an equilibrium constant $K = \frac{C_{O^{2-}}}{P_{CO_2}}$ that Dubois (11) has found equal to 10^{-6} .

The solubility of CO_2 in carbonates has been measured

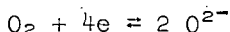
$$\frac{C_{O^{2-}}}{P_{CO_2}} = 10^{-6}$$

In these formulas the pressures are expressed in atmospheres and the concentrations of solutions in molarities.

A more recent work of Busson and Palons (12) on the potential at zero current of the oxygen electrode in the carbonates has made it possible to establish with precision the constant of equilibrium to be $K = 6$.

A solution of molten carbonates can be defined by the pO^{2-} , the negative logarithm of the concentration of ions O^{2-} .

The function of the oxygen electrode in the molten carbonates produces some O^{2-} ions.



In the vicinity of the oxygen electrode, the concentration of O^{2-} ions increases and this increase, inasmuch as it is not counter-balanced by diffusion, produces a polarization of the cell which can be called acidity polarization.

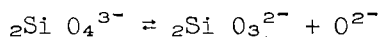
To bring CO_2 to the oxygen electrode, is to counter-balance the production of O^{2-} through the contribution of the acid part of the solvent, which as the effect of maintaining the pO^{2-} at a high value. This is a buffer effect. This effect may be visualized through Fig. 1. The diagram represents potentials of the oxygen and hydrogen electrodes as a function of pO_2 . The straight lines AC and BD are parallel and of slope $\frac{RT}{2F}$. The potential at zero current is the thermodynamic cell potential equal to AB and CD. If the hydrogen electrode operates at $pO^{2-} = 0$ and the oxygen electrode at $pO^{2-} = 6$, the potential of the cell is reduced to EB and the overpotential of acidity polarization is AE-A 600°. This overpotential is at the maximum of approximately $83 \text{ mV} \times 6 = 500 \text{ mV}$.

The pO^{2-} of the electrolyte of the cell can also vary at the fuel electrode through a contribution of CO_2 or of other products or where the pressure of CO_2 in the atmosphere rises above the electrolyte.

It is thus very important, in order to obtain a cell which operates in all circumstances, to maintain the pO^{2-} of the electrolyte constant on all parts of the cell.

Through association with the phenomena observed in aqueous solutions, we shall use weak acid systems relative to the solvent.

The orthosilicate metasilicate system fits very well:



The same applies to other salts exchanging the O^{2-} ion.

Our research has brought us to a much more simple and industrially profitable system. It is the water system.

3. WATER IN MOLTEN CARBONATES

Water has the properties of a weak acid in molten carbonates.

The properties of water may be summarized by the two equilibrium reactions:



The constants K_A and K_B are arranged to correspond respectively to these equilibria according to the relations:

$$\frac{P_{\text{CO}_2} \cdot C_{\text{OH}^-}^2}{P_{\text{H}_2\text{O}}} = K_A \quad [5]$$

$$\frac{P_{\text{H}_2\text{O}} \cdot C_{\text{O}^{2-}}}{C_{\text{OH}^-}^2} = K_B \quad [6]$$

These relations imply that the chemical potential of the solvent is constant, that is

$$C_{\text{OH}^-} \ll C_{\text{CO}_3^{2-}} \quad [7]$$

In an acid environment, the pressure of CO_2 determines the equilibrium potential, K being the equilibrium constant [1].

$$E = E_0 + \frac{RT}{4F} \log P_{\text{O}_2} + \frac{RT}{2F} \log P_{\text{CO}_2} + \frac{RT}{2F} \log K \quad [8]$$

In the presence of a water system, the potential of the oxygen electrode is given by the relation:

$$E = E_0 + \frac{RT}{4F} \log P_{\text{O}_2} + \frac{RT}{2F} \log P_{\text{H}_2\text{O}} - \frac{RT}{F} \log C_{\text{OH}^-} + \frac{RT}{2F} \log K_B \quad [9]$$

By varying the OH^- concentration and the partial pressures of water and oxygen in the atmosphere in equilibrium with the molten carbonates, we have shown that $p K_B$ is close to 5. We conclude that $p K_A = p K - p K_B = 1.5$ (by taking the reference states of gases at a pressure of one atmosphere).

There is a constant contribution of water vapor at the hydrogen electrode. On the oxygen electrode the contribution of water vapor has the effect of maintaining the basic electrolyte at a determined $p \text{O}_2$ (below 6.2).

4. APPLICATION TO FUEL CELLS

The properties of a water system in carbonates have important consequences on the functioning of cells. They allow a reduction of the acidity polarization as does the carbon dioxide fed with oxygen. But as it was demonstrated by Hart (13), the use of carbon dioxide constitutes a heavy burden from an industrial point of view whereas the use of water would be much easier and cheaper.

In comparing the properties of similar elements of a cell fed on oxygen without any addition, with carbon dioxide and with water vapor, we were able to realize that the performances due to the addition of water are the best (Fig. 2).

The polarization is not only diminished by the contribution of water vapor (potential of zero current near 1 volt instead of 0.7 volt) but the current at the same cell potential is very superior to that obtained with the use of CO_2 . This phenomenon seems to be comparable with the increase of fluidness of molten carbonates in the presence of water.

Finally, the action of water as a weak acid allows the use of fuel gas containing carbon dioxide with an hydrogen electrode of porous material. Indeed, let us consider a cell functioning with a water pressure of 0.3 atm, in an hydroxyl ion environment.

Equation [5] gives 0.015 atm as a value of $p \text{CO}_2$ in equilibrium. Consequently, any fuel gas containing a weaker carbon dioxide partial pressure may be used without the risk of modifying the $p \text{O}_2$ of the electrolyte.

5. MAKING OF PROTOTYPES

The preceding studies have first lead to tests on elements of cells of a few watts.

We are presently constructing several prototypes of a power close to 1 kw which vary in their geometric conception (vertical or horizontal electrodes) but have the same electrochemical conception.

The materials used are steel (25% Cr, 20% Ni) and dense alumina for the containers, thin sheets of palladium (50 microns) of an alloy of 24% silver-76% palladium for the fuel electrodes and silver and porous steel for the air electrodes. The electrolyte is a ternary eutectic of lithium, sodium and potassium carbonates functioning at 600°C. The fuel is a gas obtained through the reforming of natural gas and the oxidant air contains from 10 to 30% of water vapor.

The gases are fed at a pressure slightly higher than atmospheric.

Figures 3 and 4 are photographs of prototype elements with horizontal and vertical electrodes.

Naturally, these prototypes must be placed in an oven because their dimensions are too small to be autothermic.

The prototypes will give rise to a technico-economical study aimed at searching for the place of this system in the industrial production of electrical energy.

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Mmes: Busson

Jacquin

Palons

Messrs: Barde

Dubois

Heuze

Legrauche

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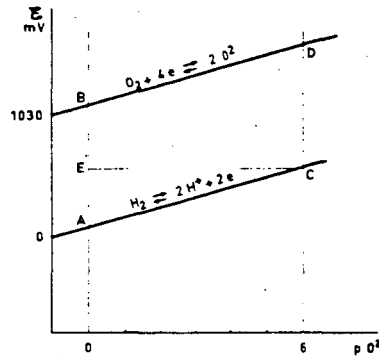
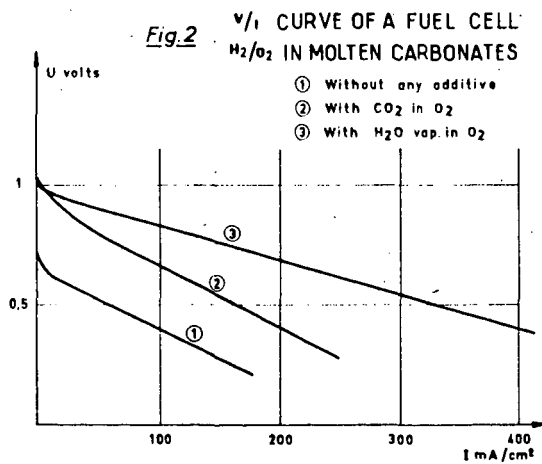


Fig. 1 THERMODYNAMIC EQUILIBRIUM
DIAGRAM IN MOLTEN
CARBONATES



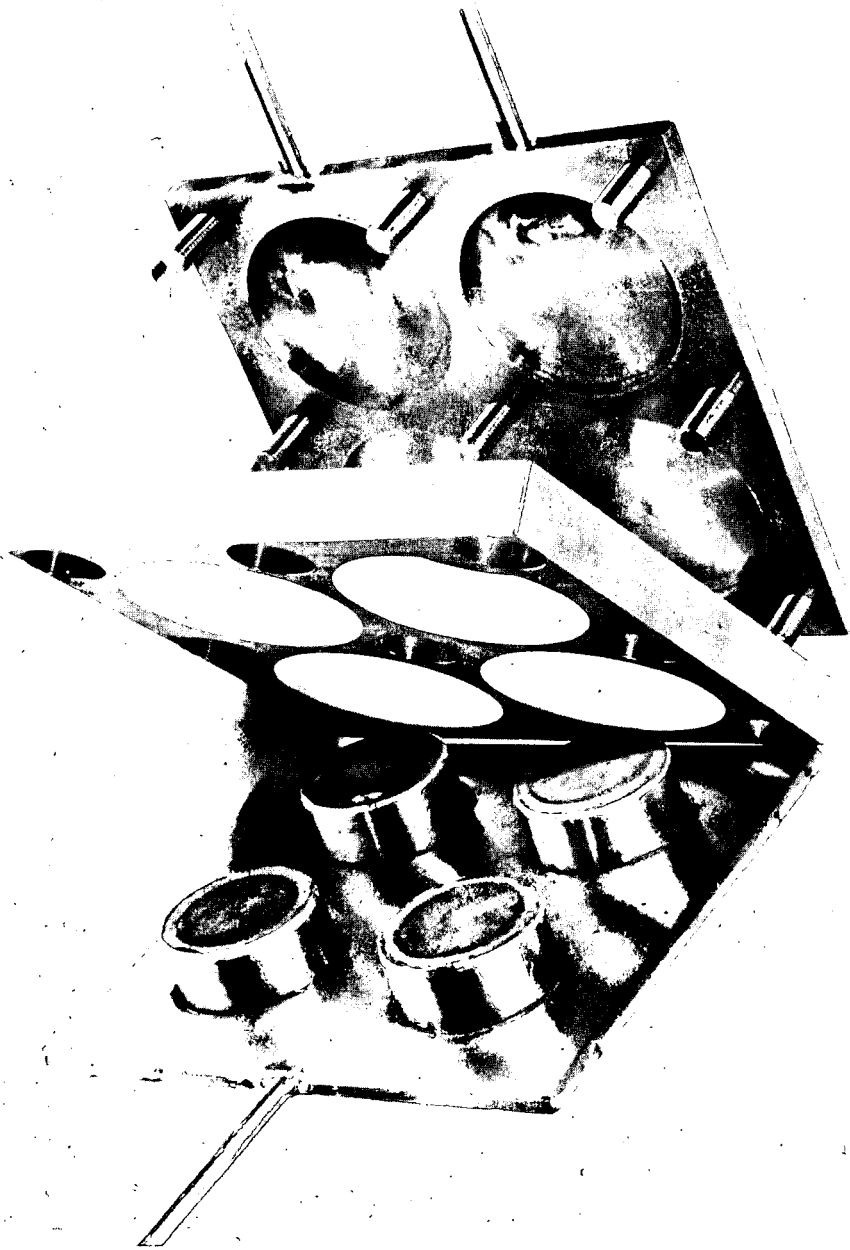


Fig. 3.-HORIZONTAL ELECTRODES PROTOTYPE

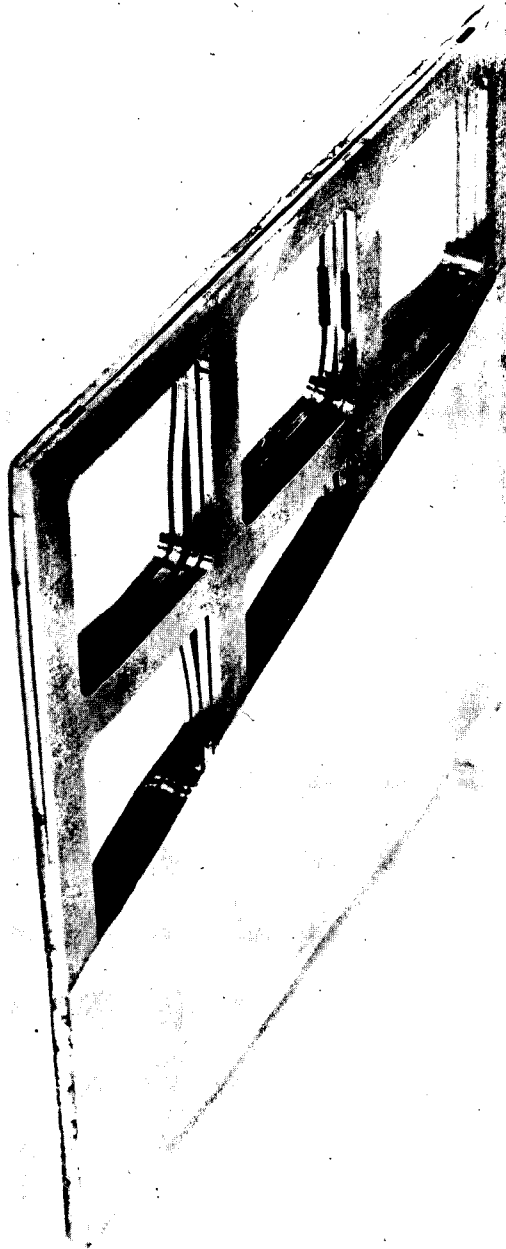


Fig. 4.-VERTICAL ELECTRODE PROTOTYPE